

Auxiliary Material for EPAPS:

Selective probing of charge and spin relaxation dynamics in the bulk and surface of a topological insulator

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SI I. Detailed Experimental Method

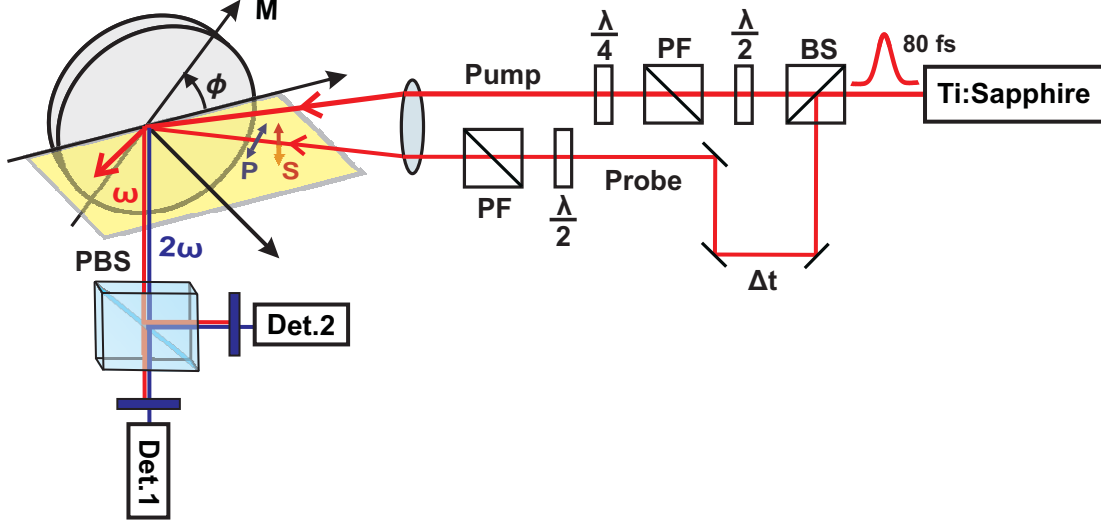


FIG. S1. Schematic of the experimental layout showing the paths of the pump and probe beams. The path of the fundamental (ω) and second harmonic (2ω) beams are shown in red and blue respectively. The probe is time delayed from the pump by using a delay stage. Optical elements are denoted as follows: polarizing beam splitter (PBS), quarter- or half-wave plate ($\lambda/4$ or $\lambda/2$), beam splitter (BS), and polarization filter (PF). Wavelength filters, used only for SHG experiments, are drawn as flat blue strips. The detectors are either Si photodiodes (for fundamental) or calibrated photo-multiplies tubes (for SHG). ϕ denotes the angle between the scattering plane and M, a mirror plane of the Bi_2Se_3 crystal.

The experimental geometry is shown schematically in Fig. S1. Ultrashort laser pulses with a center wavelength of 795 nm ($\hbar\omega = 1.56$ eV) and a duration of 80 fs at FWHM were generated from a Ti:sapphire oscillator. The 80 MHz repetition rate was reduced to 1.6 MHz by a pulse picker to avoid sample damage via cumulative heating, and the maximum laser fluence of 0.4 mJ/cm^2 was well below the damage threshold. A beam splitter was used to split the beam into a pump beam and a weaker probe beam. Using a half-wave plate and a polarizing filter, the probe beam was linearly polarized in the scattering plane (p -polarized) while the pump beam was either linearly polarized (s or p) or circularly polarized using a quarter-wave plate for spin excitation measurements. Experiments were performed in an enclosed, dark box to avoid stray light. Both pump and probe beams were focused roughly to a $20 \mu\text{m}$ $1/e^2$ spot size on the sample. The incident angle of the

pump onto the sample surface was either 0° (normal) or 60° (oblique) while the incident angle of the probe was fixed at 45° . Specularly reflected probe photons at the fundamental frequency (ω) were detected using Si photodiodes while reflected probe photons at the second harmonic (2ω) were selectively isolated through both absorptive and interference spectral filtering and detected using calibrated photomultiplier tubes sensitive to 3.12 eV photons. For fundamental probe measurements (Fig.1, main text), the intensity of the pump beam was modulated at a rate of 100 kHz using a photo-elastic modulator (PEM). Standard lock-in techniques, locked-in to the PEM frequency, were then used to determine the change in reflectivity of the reflected fundamental probe beam. The PEM and lock-in techniques were not necessary for SHG measurements due to a much greater fractional change in reflectivity $\Delta I(2\omega)/I(2\omega)$ (Fig.3(b), main text). The much greater $\Delta I(2\omega)/I(2\omega)$, on the order of 10^{-1} , is typical of an SHG measurement (e.g. [29]). For excitations by a linearly polarized pump, a polarizing beam splitter (PBS) was used to separate the reflected probe beam into s or p polarized photons. For Kerr rotation measurements, a balanced detection scheme was used which consists of rotating the PBS by 45° such that when there is no Kerr rotation so that reflected light is purely p or s polarized, equal intensity is measured in each detector. Thus, any rotation in the polarization of the incoming p -polarized probe light was manifested as a difference in the intensities measured by the two detectors.

Single crystals of lightly ($\sim 0.1\%$) As doped Bi_2Se_3 were grown by melting a 10 g stoichiometric mixture of Bi and Se shot with trace amounts of As powder in an evacuated quartz tube at 850°C . After 12 hours at this temperature, the mixture was cooled to 720°C over 2 hours, then slowly cooled to 650°C over 2 days. The batch was annealed at 650°C for 2 days then furnace cooled to room temperature.

Crystal orientation was determined by X-ray diffraction using a Bruker D8 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) and a two-dimensional area detector. Samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Nicolet Magna 860 FTIR Spectrometer. The plasmon resonance was measured to be $f_p = 1.67 \times 10^{13} \text{ Hz}$, corresponding to an electron density of $n_e = 4.33 \times 10^{17} \text{ cm}^{-3}$ in a free electron model. Actual values of the carrier density of these samples obtained in transport measurements are closer to $3.5 \times 10^{19} \text{ cm}^{-3}$ [12]. All samples were cleaved along the (111) planes in air at room

temperature prior to measurement, revealing a flat shiny surface.

SI II. Fit results for pump-probe data

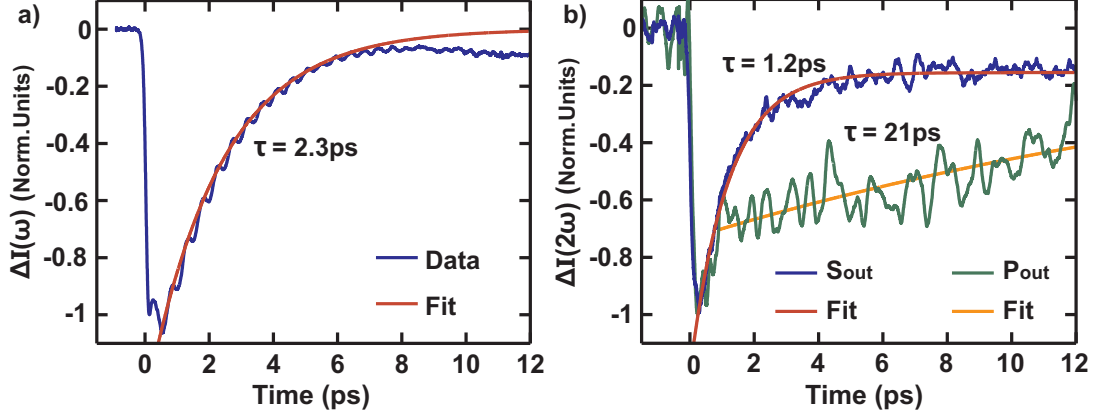


FIG. S2. a) The change in reflectivity of p fundamental probe photons following a p pump pulse. The red line is a fit to a single exponential decay function with decay constant (τ). b) Pump induced change in SHG intensity for p -in s -out (blue) and p -in p -out (green) probe photons. Both traces were taken at $\phi = 90^\circ$. The red and orange lines are single exponential fits to the corresponding data with (τ) as the decay constant.

SI III. Angular dependence of raw un-normalized SHG pump-probe data

The SHG intensity $I(2\omega)$ from Bi_2Se_3 (111) depends on the orientation ϕ [Fig. S1] of the light scattering plane relative to the crystal mirror plane through the relations:

$$\begin{aligned} I_{PS}(2\omega) &= |a \sin(3\phi)|^2 \\ I_{PP}(2\omega) &= |b + a \cos(3\phi)|^2 \end{aligned} \quad (1)$$

where subscripts on the intensity denote the input and output polarizations of the probe beam and a and b are linear combinations of $\chi^{(2)}$ and $\chi^{(3)}$ $\varepsilon(0)$ tensor elements that describe the in- and out-of-plane components of the surface response respectively [22]. In order to study the dynamics of these components, we measure the p pump induced change in SHG

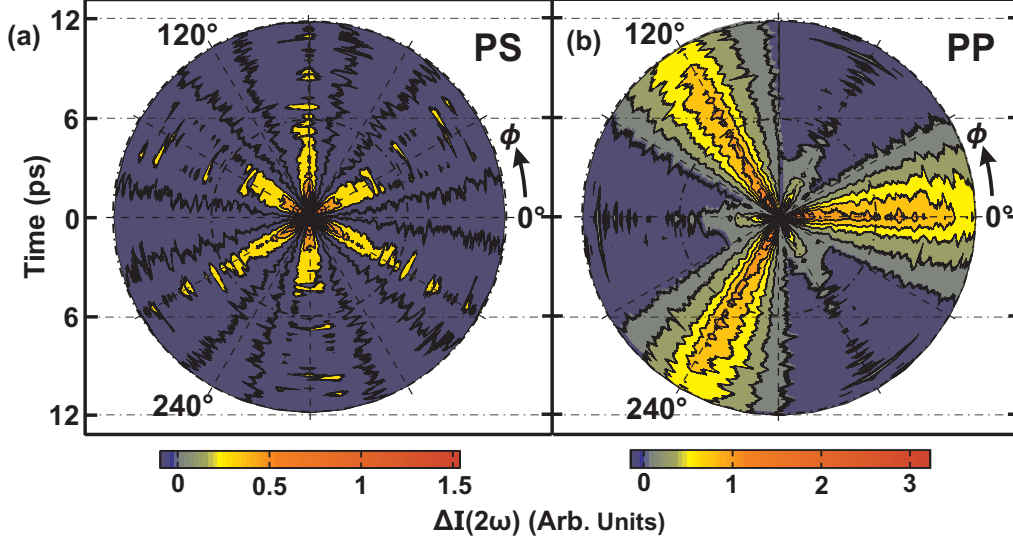


FIG. S3. a) p pump induced change in reflectivity SHG intensity as a function of sample angle ϕ measured with p -in s -out and (b) p -in p -out probe photons.

intensities $\Delta I_{PS}(2\omega)$ and $\Delta I_{PP}(2\omega)$ over the complete range of ϕ . The raw un-normalized data is plotted in Fig. S3 with time in the radial direction. The color scale represents the magnitude of the change in the SHG intensity $\Delta I(2\omega)$. To directly compare the decay rate of $\Delta I(2\omega)$ at different values of ϕ , it is essential to normalize each trace by its peak value. For example, the time-resolved un-normalized signal for $\Delta I_{PS}(2\omega)$ in Fig. S3a shows a six fold rotational symmetry because the magnitude of $\Delta I_{PS}(2\omega)$ has a $|\sin(3\phi)|^2$ dependence even though the decay rate is ϕ independent. To directly visualize the ϕ dependence of only the decay rate and not the magnitude [Fig.2a main text], we must therefore normalize each trace to its peak value.